

PROCESS FOR THE TREATMENT OF WASTE GAS AND UNIT SUITABLE
FOR USE THEREIN

The present invention pertains to a process for the treatment of waste gas. It
5 also pertains to a unit suitable for use therein.

With increasingly stringent environmental regulations, the requirements as to
the contaminant content of gaseous media, in particular gaseous media to be
vented into the atmosphere, further indicated as waste gases, become ever
10 more stringent. Accordingly, processes and apparatus are being developed to
reduce the content of objectionable components in waste gases. Such removal
can be carried out by adsorption using an adsorbent, by catalytic conversion, or
by a combination of these two processes.

15 Waste gases from which undesired components are removed by using an
adsorbent, via catalytic conversion, or by a combination of these processes
include engine exhaust gases, in particular diesel and gasoline engine exhaust
gas.

20 Diesel engines are equipped with an oxidation catalyst to control hydrocarbon,
carbon monoxide, and part of the particulate emissions. However, these
catalysts only function optimally above a certain temperature, indicated as the
"light-off temperature", that is, the temperature above which the catalytic
converter converts 50% of the incoming compound. Therefore, in diesel engines
25 the catalyst is often preceded by an adsorbent, which acts to adsorb unburned
fuel hydrocarbons at low exhaust gas temperatures, such as during cold start or
partial engine load operation, and releases them when the catalyst has reached
the higher light-off temperature to effect oxidation.

An additional use of adsorbents in diesel exhaust gas treatment is the following.

Inherent to the technology, diesel engines are operated at a high air-to-fuel ratio, which leads to relatively high NO_x formation. Reduction of NO_x to N_2 requires a temporarily fuel rich operation. WO 96/39244 of Johnson Matthey describes the use of an adsorbent in diesel engines, wherein the adsorbent adsorbs unburned fuel at lower temperature, and releases it at higher temperature. The release of unburned fuel causes a temporary increase in fuel concentration, which leads to increased conversion of NO_x to N_2 . NO_x may be converted via NO_x catalysts and NO_x trap catalysts.

Conventional gasoline engines operate in fuel rich mode and the environmentally critical compounds, viz. hydrocarbons, CO, and NO_x are oxidized and reduced, respectively, by today's standard three-way conversion catalyst systems (TWCs). Nevertheless, also in gasoline engines, cold start emissions can be reduced by in-line adsorbent devices as discussed above. Additionally, increased attention to fuel economy is leading to the development of fuel-lean gasoline engines, the exhaust characteristics of which are to a certain extent comparable to those of diesel engines, e.g., lower exhaust temperatures and increased NO_x emissions. With this development, the adsorbents and catalysts applied for diesel emission reduction will also become attractive for gasoline exhaust applications.

Both in diesel and gasoline engines, when the exhaust temperature is high enough, the hydrocarbons in question will not be adsorbed on the adsorbent anymore, but pass directly to the catalyst(s). However, the exhaust gases, which by that time may reach temperatures of above 350°C , still encounter the adsorbent. For diesel operation, temperatures of above 350°C , more in particular between 450°C and 650°C , may be reached. For conventional gasoline operation, temperatures above 350°C , in particular of 500°C to 700°C ,

may be reached. For fuel-lean gasoline engines, the temperature is expected to be lower than for conventional gasoline engines. However, values above 350°C will still be reached.

- 5 In the art, zeolites are often used in the treatment of exhaust gases, as adsorbents or as catalyst components.

The above-discussed WO 96/39244 mentions the use of ZSM-5, ion-exchanged or metal impregnated ZSM-5, silicalite, mordenite, zeolite Y and zeolite P as hydrocarbon adsorber.

- 10 US 5,849,255 describes a catalyst for trapping diesel exhaust hydrocarbons which contains a zeolite with an average pore diameter of greater than about 0.6 nm, a Si/Al ratio over 5, and retention of the crystalline structure at a temperature of 750-850°C in air. Zeolite beta, ultra-stable zeolite Y, and UTD-1 zeolite are mentioned as examples.

- 15 EP 0 499931 describes the use of a zeolite Y with a SAR of 50 in particulate removal from diesel exhaust. US 2002-0114751 describes the use of a zeolite Y with a SAR of 50 loaded with a transition metal for this application. US 2002-0028169 describes the use of a zeolite Y with a SAR of 60 loaded with noble metal for this application.

- 20 US 6,407,032 describes a lean NO_x trap comprising barium nitrate and a zeolite Y.

- EP 0 020 799 and EP 0 003 818 disclose a process for treating exhaust gases from internal combustion engines by converting noxious components using a zeolite Y with a SAR of 4.5-35, preferably 4.5-9, a unit cell size of less than
25 24.45 Å, and a sorptive capacity for water vapour (25°C, p/p₀ 0.19) of not greater than 12 wt%.

- The zeolite used in an adsorbent should be able to adsorb the molecules in question at relatively low temperature, and release them at increasing
30 temperature. Additionally, the adsorbent should be able to withstand the very

high temperatures it meets when the engine has reached full operating temperature. As the adsorbent will be used for many years, this latter feature is of particular importance.

As indicated above, zeolites are also used in the catalysts used for treatment of exhaust gases, for example, in NO_x conversion catalysts or in oxidation catalysts. Zeolites are also used in NO_x trap catalysts, materials which trap NO_x under lean fuel conditions and release them under fuel rich conditions for conversion into N₂. In these applications also, the temperature resistance of the catalyst is of importance for the same reason as given above.

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The object of the present invention is therefore to provide a process for the treatment of waste gas, preferably engine exhaust gas, more preferably diesel or gasoline exhaust gas, wherein the waste gas is contacted with a zeolite Y with exceptional heat stability properties. Preferably, the zeolite additionally shows good catalytic and adsorbing properties.

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The zeolite Y used in the process according to the invention has a unit cell size of 24.17-24.45 Å, a water adsorption capacity ($p/p_0 = 0.2$, $T=25^{\circ}\text{C}$) of at most 5 wt.%, and a bulk silica-alumina molar ratio (also called bulk or chemical SAR) of at least 40. The use of this type of zeolite in this application leads to an adsorbent/converter with high activity in combination with long life.

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Preferably, the zeolite has a bulk SAR of at least 50, more preferably at least 60, and most preferably at least 70. The bulk SAR will generally be below 200, preferably below 170, more preferably below 140. If the bulk SAR of the zeolite is too low, the adsorption properties of the zeolite will be inadequate, while Y zeolites with a very high bulk SAR and good quality are difficult and therefore expensive to prepare.

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The framework SAR of the zeolite is preferably at least 150, more preferably at least 200.

The zeolite Y has a unit cell size of 24.17-24.45 Å. Preferably, the unit cell size is at least 24.18 Å, more preferably at least 24.20 Å, still more preferably at least 24.23 Å, and most preferably at least 24.26 Å. The unit cell size preferably is at most 24.43 Å, more preferably at most 24.36 Å, still more preferably at most 24.33 Å. If the unit cell size is above the specified value, the selectivity of the zeolite for organic compounds will decrease. The preparation of zeolites with a very low unit cell size and good quality is a costly affair.

The zeolite to be used in the present invention has a water adsorption capacity (WAC) (determined at $p/p_0=0.2$ and a temperature of 25°C) of at most 5 wt.%. Preferably, the water adsorption capacity is at most 3 wt.%, more preferably at most 2 wt.%, even more preferably at most 1.5 wt%.

It has been found that there is a strong correlation between the water adsorption capacity, the bulk SAR, and the stability of the zeolite at high temperatures. Therefore, the water adsorption capacity should be as low as possible, while the bulk SAR is as high as possible.

The WAC is determined as follows. The zeolite is pretreated to dry the material for 3 hours at 425°C, and then equilibrated at 25°C and a partial water vapour pressure of $p/p_0=0.2$.

Another parameter which may be of relevance to the Y zeolites used in the treatment of exhaust gases is the residual butanol test value of the zeolite. This value, which is determined as described in GB 2,014,970, is a measure for the adsorption of 1-butanol in competition with water, and is a measure for the hydrophobicity of the zeolite. Zeolite powder is activated for 16 hours at 300°C and slurried in a 1-butanol solution in proportions such that the slurry contains one part by weight of 1-butanol, 100 parts by weight of water, and 10 parts by weight of activated zeolite Y. After gently shaking for 16 hours at 25°C, the supernatant liquid is analysed by gas chromatography. The residual butanol test value (RBT) is defined as the weight percentage of 1-butanol remaining in solution. It has been found that if the zeolite to be used in the present invention

has a RBT of below 0.2, in particular below 0.17, more in particular below 0.15, still more in particular below 0.13, particularly attractive results are obtained.

Zeolites which meet the above requirements are known in the art. They are, e.g., described in US 4,401,566, GB 2,014,970, EP 320, 247, and WO 00/51940.

As indicated above, zeolites which meet the above requirements show a particularly high thermal stability under the high-temperature conditions which they periodically meet during use. Accordingly, they are particularly suitable for use in the treatment of waste gas according to the invention in processes where they are periodically subjected to temperatures above 350°C, more in particular in the treatment of engine exhaust gas, preferably diesel or gasoline exhaust gas, in processes where they are periodically subjected to temperatures above 350°C.

The zeolite's high thermal stability under the high-temperature conditions which it periodically meets during use can be seen from the relatively low decrease in micropore volume when the zeolite is subjected to steaming conditions which simulate the fast heating-up and long-term high temperature circumstances in engine exhaust systems.

The pore volume characteristics are obtained from the nitrogen adsorption isotherm at 78 K, which can be determined using commercially available equipment, e.g., Micromeritics A.S.A.P.-2400 or Gemini-2360. The adsorption V_a at a relative pressure P/P_0 of 0.30 is interpolated from adjacent points on the adsorption isotherm. To calculate the micropore volume, the nitrogen adsorption isotherm in the range of $P/P_0 = 0.08$ to 0.80 is converted to a t -plot using the Harkins-Jura equation given by de Boer et al. (J. Colloid Interface Sci. Vol. 21 (1966), 405), with t standing for the thickness of the adsorbed layer.

$$t (\text{\AA}) = \left(\frac{13.99}{0.034 - \log P/P_0} \right)^{1/2}$$

Since the t-plots of zeolites are slightly curved, the part of the plot used for determining the slope and the intercept has to be specified. In the present specification the range employed is from t is 3.5 Å to t is 5.3 Å. The straight line drawn through the points in this range with the aid of the least squares method has an intercept V_{mi} and a slope $\Delta V_a/\Delta t$. The micro PV is calculated using the formula: micro PV (ml/g) = 0.001547 V_{mi} .

In one embodiment of the present invention, the zeolite functions as an adsorbent which adsorbs undesired compounds, in particular organic compounds, from waste gas at low temperature, e.g., below 120°C, and desorbs them at a higher temperature, e.g., above 120°C.

This goes in particular for adsorption of undesired components from engine exhaust gases, such as unburned fuel components. For diesel exhaust, the adsorption preferably takes place at a temperature below 120°C, while the desorption takes place at a temperature above 120°C. For conventional gasoline exhaust, the adsorption preferably takes place at a temperature below 170°C, while the desorption takes place at a temperature above 170°C. For lean fuel gasoline exhaust, the adsorption preferably takes place at a temperature below 120°C, while the desorption takes place at a temperature above 120°C.

In diesel exhaust, the desorbed hydrocarbons are led to an oxidation catalyst, to a NO_x conversion catalyst, or to a NO_x trap catalyst. In conventional gasoline exhaust, they are led to a TWC catalyst system. In lean-burn gasoline systems gases can be converted by a NO_x conversion catalyst or captured in a NO_x trap instead of TWC's. The above-mentioned zeolite can also be used in said oxidation catalysts, NO_x conversion catalysts, and NO_x trap catalysts.

For use as oxidation catalyst, the zeolite is preferably provided with noble metals such as platinum, palladium, or rhodium.

For use in a lean NO_x catalyst, the zeolite is preferably provided with a noble metal of Group VIII of the periodic table of elements and/or with a non-noble metal of Group VIII of the periodic table of elements and/or with a metal of Group I. Noble Group VIII metals include platinum and palladium. Non-noble metals of Group VIII include nickel, cobalt, and iron. Copper is the most suitable metal of Group I.

For use in a NO_x trap, the zeolite is preferably provided with an alkaline earth metal such as calcium, barium, or strontium. In this technology, NO_x is first oxidised to NO₂ by catalytic metals useful for such oxidation, e.g., precious metals such as platinum, palladium, and rhodium. The NO₂ is then trapped on the surface of the catalyst in the form of a nitrate. The system is periodically operated under fuel rich conditions, which effect release of the NO_x and conversion thereof into N₂.

These catalysts are therefore preferably provided with noble metals as specified above, and a compound suitable to trap the nitrate, e.g., barium carbonate.

A combination of adsorption and catalytic conversion is also envisaged for the present invention. The present invention therefore also pertains to the use of a combination of an adsorbent and a catalyst in the treatment of waste gas, preferably engine exhaust gas, more preferably diesel or gasoline engine exhaust gas, wherein at least one of the adsorbent and the catalyst comprises the above-described zeolite. Accordingly, the present invention also pertains to a process for the treatment of exhaust gas from a diesel engine, wherein the engine exhaust system is provided with a hydrocarbon adsorbent and/or an oxidation catalyst and/or a NO_x conversion catalyst, and/or a NO_x trap catalyst, wherein the hydrocarbon adsorbent and/or the NO_x conversion catalyst, and/or the NO_x trap catalyst comprise a zeolite Y with the above properties. The present invention further pertains to a process for the treatment of exhaust gas

from a gasoline engine, wherein the engine is provided with a hydrocarbon adsorbent and a TWC catalyst or NO_x conversion catalyst and/or a NO_x trap catalyst, wherein the hydrocarbon adsorbent and/or the NO_x conversion catalyst, and/or the NO_x trap catalyst comprise a zeolite Y with the above
5 properties.

The zeolite is preferably used in the treatment of exhaust gases in the form of a thin layer on a monolithic carrier. Monolithic carriers are known in the art and include, e.g., the well-known honey-combs. The zeolite is applied onto the
10 carrier in manners known in the art, e.g., by contacting the carrier with a slurry of the zeolite, followed by drying and calcining. This process is often indicated as preparing a wash-coat.

Accordingly, the present invention also pertains to a unit suitable for the
15 treatment of exhaust gas as described above, which comprises a zeolite with the above-mentioned properties.

The unit preferably is a monolith at least part of the surface of which is coated with the zeolite. Optionally, the monolith can comprise one or more of the metal components indicated above.

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EXAMPLE

The hydrothermal stability of zeolites Y1 to Y4 was determined by steaming the zeolites for 5 hours at 850°C under a flow of air containing 10 vol% H₂O.

The relative crystallinity was determined by taking the crystallinity of the zeolite
25 after steaming relative to the crystallinity before steaming. The crystallinity of the zeolite was determined by measuring the XRD peak surfaces relative to an internal zeolite Y standard.

The relative crystallinity after steaming was taken as a measure for the hydrothermal stability: the higher the relative crystallinity, the higher the hydrothermal stability.

The relative crystallinity of the different zeolites is shown in Table I.

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Zeolites Y1, Y2, and Y3, having a SAR in the range 4.5-35, a unit cell size of less than 24.45 Å, and a WAC of not greater than 12 wt%, are representative for the zeolites of EP 0 020 733 and EP 0 003 818.

Zeolite Y4 is a zeolite according to the present invention.

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As can be seen from Table I, the zeolite according to the present invention has a higher heat stability than the zeolites representative for EP 0 020 733 and EP 0 003 818.

15 Table I

Zeolite	Unit cell size (Å)	WAC (p/p ₀ =0.2, T=25°C)	Bulk SAR	Relative crystallinity (%)
Y1	24.35	5.7	12	89
Y2	24.33	4.6	16	91
Y3	24.31	1.9	29	94
Y4	24.29	1.3	56	99